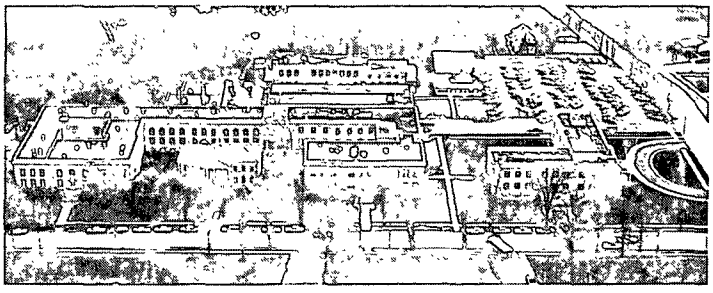

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THE EVOLVING MODELS OF THE STRUCTURES OF CELLULOSE

RAJAI H. ATALLA

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The Evolving Models of the Structures of Cellulose

Rajai H. Atalla

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THE EVOLVING MODELS OF THE STRUCTURES OF CELLULOSE

RAJAI H. ATALLA
The Institute of Paper Chemistry
Appleton, WI 54912 U.S.A.

Abstract The observations which have, in recent years, required reassessment of the structural models of cellulose are reviewed, and the criteria which now must be met by any acceptable model are discussed. It is noted that among structures based on diffractometry alone, there are many inconsistencies, even though they all represent approximations of varying degrees of adequacy. The spectroscopic investigations carried out over the last two decades, based primarily on Raman spectroscopy and CP/MAS ^{13}C NMR, have required reexamination of some of the assumptions implicit in the structural models. The spectroscopic results point to two essential modifications of the assumptions which underlie interpretations of the diffractometric data. The first is that nonequivalence of adjacent anhydroglucose units in a molecular chain be admitted, by relaxation of the constraint of $P2_1$ symmetry, thus allowing the dimeric anhydrocellobiose to be the basic repeat unit of physical structure. This is applicable to both celluloses I and II, and would inherently also admit the possibility of different conformations of the cellulose chains for the two allomorphs. The second modification requires acknowledgment of the composite nature of native celluloses, as revealed by ^{13}C NMR, and, thus, introduction into the analysis of crystallographic information the possibility that the crystalline domains represent a superlattice in which two complementary and similar types of unit cells can coexist. The models of cellulose which emerge from these amendments of structural assumptions correspond to a chain with alternating left-handed and right-handed glycosidic linkages, in sequence, between successive anhydroglucose units. These configurations of the glycosidic linkages are qualitatively similar to those which occur in the structures of cellobiose and methyl-β-cellobioside, respectively. They represent

relatively small departures of the dihedral angles defining the linkage from the parameters of a twofold helix; the degree of departure from the twofold helix is larger for cellulose II than for cellulose I. Finally, the relevance of the present analysis to studies of the structures of other polysaccharides is considered. It is suggested that whenever the diffractometrically based structural models are not readily reconciled with other aspects of the phenomenology of a particular biopolymer, it is worthwhile to consider whether the assumptions, particularly with respect to symmetry, might not be relaxed to allow limited deviations. Furthermore, it is suggested that for the β 1,4 linked hexosans, serious consideration needs to be given to the factors which were found to be important in the analysis of the models of cellulose.

INTRODUCTION

Students of ancient mythology allude to the role of myths in early cultures as constructs which aided people in organizing their experience of reality. In this respect, models of molecular structure are also myths, for above all, they provide a basis for organizing primary data from a variety of sources, all of it related to structure in one way or another. Ancient myths evolved as they passed from one culture to another, and from one civilization to another, their adaptations, in the main, reflecting the new experiences of the later cultures. In the same way structural models undergo evolutionary change as the body of primary observations they are called upon to integrate expands beyond the domain of the data giving form to their first conception. In this report we review, in this perspective, recent refinements of the structural models of cellulose to integrate the results of new classes of observations made in the course of the last two decades. In the context of these

proceedings it is also in order to inquire into the degree to which the considerations which led to revision of the models of cellulose are relevant to the study of other polysaccharides, particularly the β 1,4 linked hexosans.

Until recently, the primary sources of structural information were x-ray and electron diffractometric measurements. Over a period of approximately 60 years, diffractometric studies of increasing sophistication have been undertaken in search of more precisely defined structures for cellulose. A number of models of structure which can rationalize the diffractometric data to varying degrees have been developed. It is not clear, however, that the data allow discrimination between many of the structures which have been proposed. Furthermore, questions have arisen concerning the models based on diffractometry because they do not provide a basis for integrating other primary observations of phenomena which are quite sensitive to structure.

The criterion for acceptability of structural models has necessarily been extended as new spectroscopic studies have been undertaken and as they have resulted in measurements of quantities that are very sensitive to structural parameters. It must now be required of the models that they possess a significant measure of utility as the basis for organizing, explaining and predicting as wide a variety as possible of these new experimental measurements related to structure. The inadequacy of the models based on diffractometry with respect to this criterion has provided the impetus for the refinements of the models alluded to above.

The author's perspective in this regard has grown out of the effort over two decades to interpret first the Raman spectra and, more recently, the CP/MAS ^{13}C NMR spectra of a wide range of celluloses.[1,2]

It is well to note at the outset that three levels of structure need to be defined. The first is that of the chemical structure reflected in the pattern of covalent bonding, which is no longer in question in the case of cellulose. The next level is that of the organization in space of the repeat units in an individual molecule. This level is most directly related to spectroscopic measurements, where the energy levels between which transitions are observed are determined by the values of the internal coordinates which define molecular conformations. The third level of structure is that reflecting the arrangement of the molecules relative to each other in a particular state of aggregation. This is the level of structure probed by diffractometric measurements which are inherently most sensitive to order in a three-dimensional lattice.

In the following we present brief summaries of key findings based on diffractometry and on the different spectroscopic techniques. We also discuss the refinements of the structural models which seem necessary to reconcile the results, taking into consideration, as well, information derived from conformational analysis and from the study of oligomeric compounds.

DIFFRACTOMETRIC STUDIES

The primary difficulty in structural studies of polymeric

fibers is that the number of reflections usually observed in a diffraction pattern is quite small. It becomes necessary therefore to complement the diffractometric data with information from other sources. These usually include assumptions about the nature of the monomeric entity, structural information from homologues, and any available information about the symmetry of the structure.[3]

In the case of cellulose, it has been customary to assume that the repeat unit is anhydroglucose, and that the structures possess the symmetry of space group $P2_1$. Yet even with this additional information, the structures derived from diffractometric data have varied considerably. This is perhaps best illustrated by examining the structures reported for cellulose I by Gardner and Blackwell[4] and by Sarko and Muggli.[5] As French has noted,[6,7] when the same convention is applied in defining the axes of the crystal lattice, the structure most favored in one analysis is strongly rejected in the other, and vice versa. Furthermore, neither of the parallel structures is strongly favored over yet a third, an antiparallel structure.

The applicability of the symmetry of space group $P2_1$ has also been the subject of much discussion. In an electron diffractometric study of a number of celluloses, Hebert and Muller[8] confirmed the findings of earlier investigators who found no systematic absences of the odd order reflections forbidden by the selection rules of $P2_1$, and concluded that the cellulose unit cells do not belong to that space group.

Some uncertainties have remained in yet another area of structural investigation, that is, the relationship to each other of the structures of the two most common allomorphs of cellulose, corresponding respectively to native (I) and regenerated or mercerized (II) celluloses. In comparisons of the structures of celluloses I and II Petitpas et al.[9] have concluded that the chain conformations are different, while Norman,[10] on the basis of an equally comprehensive study, found the conformations of the chains to be the same. More recently, it has been proposed that the primary difference between celluloses I and II is that the former possesses a parallel arrangement of the polymeric chains while the latter possesses an antiparallel structure.[11] This proposal requires rearrangements of the molecules on a large scale, and is not consistent with the speed of the lattice conversion during mercerization. Given the limited degree to which the diffractometric data permit discrimination, as noted by French,[6] the proposal has little to recommend it.

In summary, it can be said that a number of structures, all ribbon-like and possessing $P2_1$ symmetry have been proposed for cellulose. Though there is little consensus about their validity, it is quite likely that, apart from the question of chain polarity, they are all approximately correct. The need for further refinement thus arises not from the diffractometric studies, but rather from the need, noted above, for a model that provides a basis for rationalizing spectroscopic observations as well as the diffractometric results.

STRUCTURES OF CELLULOSE

SPECTROSCOPIC STUDIES

Two types of spectroscopic investigation have been applied to cellulose for the first time during the past two decades. These are Raman spectroscopy and solid state ^{13}C NMR using the CP/MAS technique. Both have given cause for questioning the assumptions, which have been incorporated in the crystallographic studies, about symmetry and about the identity of the basic repeat units in the molecular chains. And while in this instance spectroscopic measurements cannot provide direct information concerning the coordinates of atoms in the unit cells, they establish criteria that must be met by any structural model before it can be regarded as adequate.

RAMAN SPECTROSCOPY

Raman spectroscopy is the common alternative to infrared spectroscopy for investigating vibrational spectra; it has enjoyed a significant revival since the development of laser sources for excitation. Its key advantage in the study of cellulose is that it is primarily sensitive to the skeletal vibrations of the molecular chain, the mode of packing in the lattice having only secondary effects on the key features in the spectra.

From a detailed comparison of the spectra of celluloses I and II, particularly in the low frequency skeletal bending region, Atalla[12] concluded that the molecular chains must possess different conformations in the two allomorphs, in addition to belonging to different lattices. This led to

the linkage from the values prevailing in a twofold helical structure. The degree of departure from the parameters of a twofold helix is seen as somewhat larger for cellulose II than for cellulose I.

SOLID STATE ^{13}C NMR SPECTROSCOPY

Studies of the high resolution ^{13}C NMR spectra of celluloses have added important insight into the subtleties of the structures. In this technique, cross polarization (CP) is used to enhance the ^{13}C signal, high power proton decoupling to eliminate dipolar couplings with protons, and magic angle spinning (MAS) of the sample, about a particular axis relative to the field, to eliminate chemical shift anisotropy. The spectra are of sufficiently high resolution that chemically equivalent carbons which occur in magnetically nonequivalent sites can be distinguished.

Though a number of investigators have used this technique,[19-23] we focus on the studies by VanderHart and Atalla[24,25] because of the structural questions they addressed. For all of the celluloses of interest here, the spectra showed resonance multiplicities for chemically equivalent carbons, and the primary objective has been to reconcile these multiplicities with the structural models.

The spectra of high crystallinity samples of cellulose II show clear splittings of the resonances of C4 and C1. These have been interpreted as evidence of the nonequivalence of glycosidic linkages postulated on the basis of the vibrational spectra in the OH region. More generally, the

differences throughout the ^{13}C NMR spectra between those of native celluloses (I) and those of regenerated or mercerized celluloses (II) are consistent with the proposal of two distinct conformations being predominant in these two general classes of celluloses.

Perhaps the most significant new information derived from the ^{13}C NMR spectra is that relating to the native celluloses. The spectra reveal multiplicities that cannot be interpreted in terms of a unique unit cell, even though they arise from magnetically nonequivalent sites in crystalline domains. The narrow lines observed have relative intensities which are neither constant among the samples of different native celluloses, nor in the ratios of small whole numbers as would be expected if they arose from different sites within a relatively small unit cell.

VanderHart and Atalla proposed that native celluloses are composites of two distinct crystalline forms. Spectra of the two forms were derived from linear combinations of the spectra of native celluloses which contain the two forms in different proportions. The two forms were designated I_α and I_β. The I_α form was found to be dominant in celluloses from lower plant forms and bacterial celluloses, while the I_β form was found dominant in celluloses from higher plants.

More recently, VanderHart and Atalla[26] have presented the results of magnetic relaxation and spin diffusion studies which confirm the primary hypothesis of two distinct crystalline forms. On the basis of further studies of the Raman spectra Atalla[27] concluded that the two forms consist

of molecular chains which have the same molecular conformation. Wiley and Atalla[28] presented further evidence that the molecular conformations are the same, together with evidence that the key difference between the two forms lies in the different patterns of hydrogen bonding between the molecular chains.

REPRESENTATIVE SPECTRA

The nature of the primary information provided by the spectroscopic measurements is best demonstrated by examination of representative spectra. Figure 1 shows spectra reported by Wiley and Atalla,[28] and provides comparison of the Raman spectra of cellulose fibrils from Valonia ventricosa and from ramie, together with a mercerized ramie fibril. The spectra were recorded using the Raman microprobe, with the polarization of the exciting laser oriented parallel to the axes of the fibrils.

Two comparisons are of interest. The spectra of the native ramie and the mercerized ramie reveal the significant differences, particularly in the low frequency region (250-700 cm^{-1}), which led to the conclusion that the molecular conformations are indeed different in these two allomorphs. The spectra of the Valonia and the native ramie, in contrast, are very similar in the low frequency and the fingerprint region (250-1500 cm^{-1}); the indication of greater linewidth in the spectra of the ramie reflects the effect of the smaller lateral dimensions of the primary crystalline domains. The similarities between the spectra

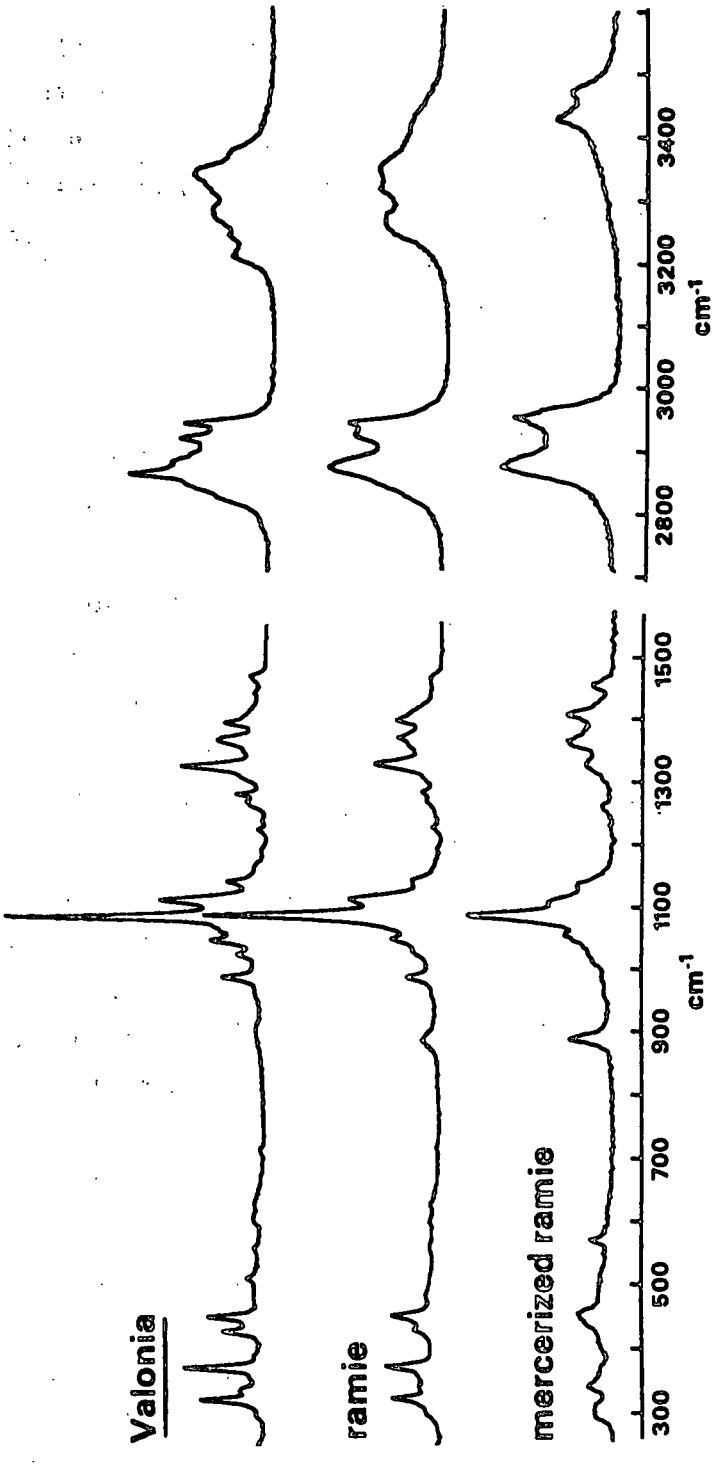

Figure 1. Raman spectra of fibrils of native and mercerized celluloses, acquired with the Raman microprobe with the electric vector of the exciting laser radiation parallel to the fibril and molecular axes.

are the basis for the conclusion that the two crystalline forms which coexist in native celluloses possess molecular chains with essentially identical conformations. The OH region (3100-3650 cm^{-1}) in the spectra, on the other hand, reveals significant differences between Valonia and ramie. It is this difference which suggested that though the two forms possess chains with the same conformation, they must be hydrogen bonded in different patterns. It is interesting to note, also in this region, the two sharp bands in the spectrum of the mercerized ramie; these have been associated with the isolated intramolecular hydrogen bonds which occur in this structure.

Figure 2 is taken from Atalla and VanderHart,[24] and shows the complex multiplicities in the CP/MAS ^{13}C NMR spectra of the native celluloses. The spectra in this figure were the basis of the resolution into linear combinations of the spectra of two distinct crystalline forms. Figure 3 shows the two I_α and I_β, which, in linear combination can duplicate all the spectra shown in Figure 2. In addition, for comparison purposes, Figure 3 includes a spectrum of cellulose II; the splittings of the C1 and C4 resonances are part of the evidence for the nonequivalence of glycosidic linkages noted above.

PATHWAYS TO MORE USEFUL STRUCTURAL MODELS

Historically the crystallographic studies have sought the most simple model structures consistent with observations. Clearly the structures based on anhydroglucose as the repeat

unit are the most simple ones, and they can account for a significant portion of the diffractometric data. Furthermore, the data available did not provide a basis for introducing departures from the most simple models, nor suggestions for their revision. The spectroscopic studies now provide the bases for such refinements.

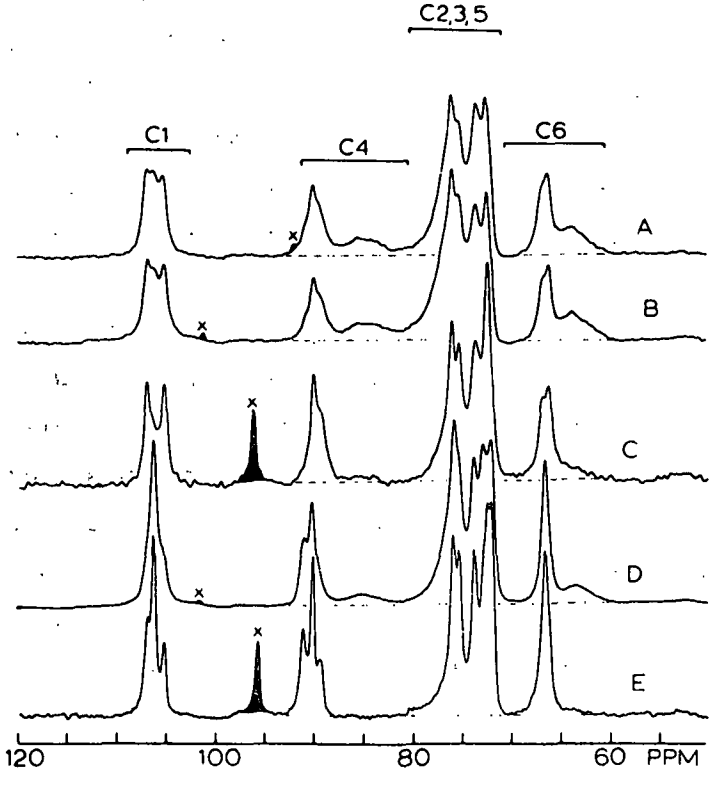

Figure 2. Solid State (CP/MAS) ^{13}C NMR spectra of native celluloses. A - Ramie; B - cotton linters; C - regenerated cellulose I; D - Acetobacter xylinum cellulose; E - Valonia ventricosa cellulose. The "X" marks the small first spinning sideband of linear polyethylene added as an internal standard its centerband at 33.6 ppm is not included in this display.

STRUCTURES OF CELLULOSE

The spectroscopic observations have structural implications at three different levels. First they suggest a complexity to the structure of native cellulose that had not heretofore been recognized. Next they point to a reality that is unusual in polymeric structures, that is, that chemically equivalent repeat units are not symmetrically equivalent. Finally they require that conformational changes be an integral part of any understanding of allomorphic transformations.

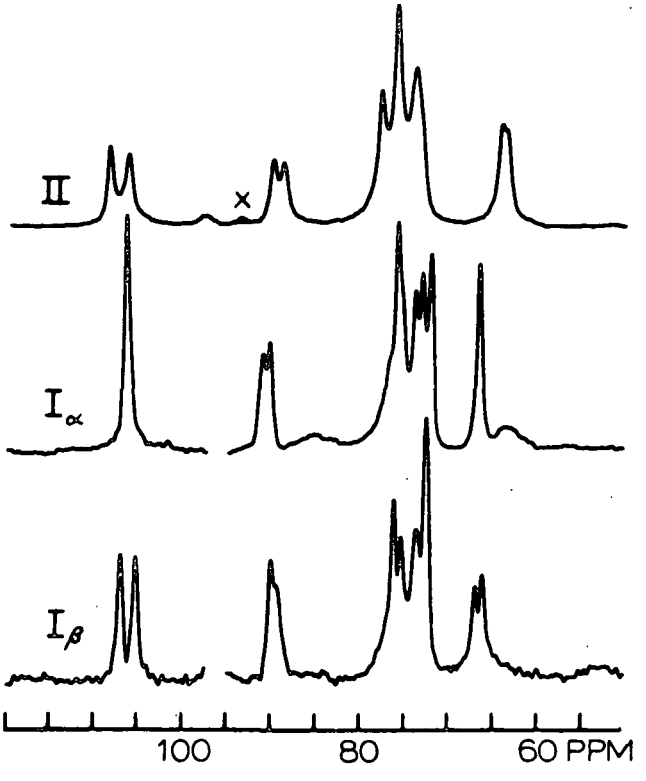

Figure 3. Comparison of the ^{13}C (CP/MAS) spectra of cellulose II and the spectra of the two crystalline forms of cellulose I, namely, I_α and I_β. An "X" or a gap mark the locations of the first spinning sideband of the linear polyethylene chemical shift standard.

It has been known for some time that celluloses from algae and from bacterial sources produce diffraction patterns that have many features in common with those of celluloses from higher plants, but that these patterns cannot be indexed as simply or on the basis of the same unit cell. This, no doubt, is a consequence of the composite nature of these celluloses as revealed by the ^{13}C NMR CP/MAS spectra. It was noted above that the two classes of native celluloses have different proportions of the I_α and I_β forms. Since these two forms have the same molecular conformations but different hydrogen bonding patterns, the coordinates of the heavy atoms in the unit cells are expected to be quite similar, but those of the hydrogens to be different. The similarities in the heavy atom locations can account for the commonalities in the diffraction patterns, while the differences in the coordinates of the hydrogen atoms are responsible for the differences between the patterns. This would account for the greater incidence of disallowed reflections in electron diffraction patterns.

It is not clear that a polymeric system with a composite structure such as that derived from the spectroscopic data represents a tractable crystallographic problem. However, an understanding of the origin of the anomalies in the diffraction patterns may suggest new approaches to interpretation of the diffractometric data.

Another important implication of the models derived from the spectroscopic data for native cellulose is that the manner of aggregation of molecular chains in the lattice may be determined more by their shape than by the hydrogen

bonding pattern. Thus, in conformational and packing energy calculations it is necessary to assign greater weight than is customary to the contributions of Vander Waals forces relative to the hydrogen bonding potentials.

The question of nonequivalence of adjacent anhydroglucose units, requiring that the repeat unit is anhydrocellobiose, is complementary to the question of nonequivalence of the glycosidic linkages. That is, one implies the other. Both, of course, are also expressions of the degree of departure from $P2_1$ symmetry. The model proposed on the basis of the spectroscopic data envisions alternating glycosidic linkages, corresponding to small left-handed and right-handed departures from a twofold helical structure. Such linkages would allow the overall structure of the chain molecule to approximate a twofold helical structure but depart sufficiently from such symmetry to allow for the nonequivalence of the adjacent anhydroglucose units. In a recent study French[7] has reported that such a structure may indeed be consistent with the diffractometric data for cellulose I. Sakthivel et al.[29,30] have arrived at similar conclusions for cellulose II.

The degree to which conformational change is involved in allomorphic transformations has also been in question. It is of interest both because it sheds light on the structural questions and because it is relevant to an understanding of the mechanisms of transformation. As noted above, the structures most recently derived from diffractometric data showed cellulose I to have a parallel arrangement of the molecules, but cellulose II to have an antiparallel

arrangement, so that the allomorphic transformation seemed to require a very significant reorganization of the molecules. But the allomorphic transformation can be complete within a few seconds during mercerization; thus, a mechanism requiring a transition from parallel to antiparallel orientation of the chains is not very plausible. On the other hand, a transformation arising from small changes in the conformations of the molecular chains, within a swollen lattice, is consistent with both the phenomenology of the transformations and the spectroscopic observations. It should be emphasized that the mechanism of the allomorphic transformation proposed on the basis of the spectroscopic data implies preservation of the nonequivalence of adjacent anhydroglucose units.

In summary then, the spectroscopic results point to two essential modifications of the basic assumptions which underlie interpretations of the diffractometric data. The first is that nonequivalence of adjacent anhydroglucose units be admitted by relaxation of the constraint of $P2_1$ symmetry. This change is applicable to the structures of both celluloses I and II, and would inherently also admit the possibility of different conformations for the two allomorphs. The second modification requires acknowledgment of the composite nature of native celluloses, and, thus, introduction into the analysis of crystallographic data the possibility that the crystalline domains represent a superlattice in which two complementary types of unit cells can coexist. A reinterpretation of the diffractometric data with these two considerations in mind seems at present the

most promising path to new models of structure which meet the criterion for acceptable structures discussed above.

OTHER POLYSACCHARIDES

Within the context of these proceedings it is clearly in order to ask whether the criterion of acceptability, which has guided our analysis of the structures of cellulose, should also be applied to the models of structure of similar polysaccharides. While a review of the status of model structures of the other polysaccharides is clearly beyond the scope of this report, it is well to consider the circumstances that would suggest a reassessment is in order. The problem in the crystallography of the polysaccharides is that the uncertainties in the structures based on diffractometry are not usually clearly set forth. And, most often, consistency with the diffractometric data is the only criterion that is considered.

The elements in the analysis of the structure of cellulose which first attracted attention to the need for reassessment were the difficulties in interpretation of the spectra. The problem of biogenesis had also remained an important one as long as the crystallographic studies suggested an antiparallel structure for native cellulose; no plausible biosynthetic mechanism could be reconciled with such a structure. It was only in consequence of these inconsistencies that the diffractometrically based models of structure were reassessed more critically.

The instance of cellulose suggests that, for the other polysaccharides also, reassessments are in order when the structural models are not readily reconciled with other aspects of phenomenology. For example, the uncertainties with respect to the adequacy of the diffractometric data as a basis for discrimination between parallel and antiparallel structures raise questions about the validity of antiparallel structures for native forms of other polysaccharides that are likely to aggregate simultaneously with biogenesis. It is not that the competence of efforts reflected in the diffractometric studies is in question, but rather that the experience with cellulose points to the inadequacy of the diffractometric data alone for the specification of a unique structure. Since few other polysaccharides have been investigated diffractometrically as frequently as has cellulose, it may be that the multiplicity of structures possibly consistent with diffractometric data is not usually so obvious.

It is also worthwhile to inquire about the specific considerations which entered into the interpretation of the spectral data for cellulose, and which led to revisions of the models of structure, and the degree to which they may be relevant to analysis of the structures of other β 1,4 linked polysaccharides. Two key factors were important in the analysis of the conformations of cellulose. The first is the high degree of overlap between the hydrogen atoms on C1 and C4 of the glycosidic linkages, of structures possessing $P2_1$ symmetry. The overlap results in two primary minima in mappings of the potential energy as a function of the dihedral

angles which define the geometry of the glycosidic linkage; the two minima correspond to the two different states of the glycosidic linkage suggested by the spectroscopioc data. The diffractometric studies had ignored this duality, and supposed the existence of only one such minimum. The second factor is the role of C6, both as a constraint on the freedom of rotation about the glycosidic linkage, and because of the possibility of the participation of the OH group in intramolecular hydrogen bonds. These same factors are clearly present in any of the β 1,4 linked hexosans. Thus, the questions which arose with respect to the diffractometrically derived structures of cellulose need to be posed with respect to diffractometrically based structures currently accepted for the analogous hexosans.

An alternative mode for posing some of the questions would be to examine the assumption, usually implicit in most crystallographic studies of polymers, that chemically equivalent repeat units are symmetrically equivalent; in the case of cellulose, the analysis of the spectra eventually led to questioning of this assumption. The problem with polysaccharides in general is that the complexity of the individual repeat units, and the large number of internal degrees of freedom, make possible local deviation from symmetric equivalence which may not be revealed in a crystallographic analysis, especially if the analysis begins with the premise that such deviations do not occur. This problem becomes particularly acute when the symmetry assumed in the analysis does indeed approximate the structure. Then for most applications the model of higher symmetry may well be

adequate. However, when such a model is not capable of reconciling other aspects of phenomenology, its validity must be questioned, as has been necessary in the case of cellulose.

This discussion has been focused on the polysaccharides which are most like cellulose, that is the β 1,4 linked hexosans. The same considerations, with the exception of those related to effects associated with C6, are also applicable to analyses of the β 1,4 linked pentosans.

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